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# Low temperature sintering of $Ba_xSr_{1-x}TiO_3$ glass-ceramic

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## Abstract

The sintering temperature of $Ba_xSr_{1-x}TiO_3$(BST) ceramic prepared by conventional method is too high (1350–1400 °C) [Mater. Sci. Semicond. Process. 5 (2003) 215] to co-fire with high-conductive and low-melting temperature conductors, such as Ag. In this paper, Ba–Sr–Ti–Pb–B–Si–O gel-glasses were prepared by sol–gel process. BST crystalline grains grew out from an amorphous gel-glass matrix at proper heat treatment temperatures. Because of the glass content, the sintering temperature of BST can be decreased below 1000 °C. Because $Pb^{2+}$ substituted $Ba^{2+}$ and $Sr^{2+}$ in the perovskite lattice forming $PbTiO_3$. The Curie temperature of BST glass-ceramic was higher than that of the pure $Ba_xSr_{1-x}TiO_3$ ceramic. The effect of the amount and composition of Pb–B–Si–O glass on BST was studied and presented in this paper.

*Keywords:* D. Glass-ceramic; BST; Low-temperature sintering; Sol–gel

## 1. Introduction

Barium strontium titanate ($Ba_xSr_{1-x}TiO_3$, BST) has been widely used as capacitor, piezoelectric transducer, optical signal processing, and memory cell capacitors in dynamic random access memory (DRAM) due to its high permittivity ($\varepsilon$), low dielectric loss ($\tan\delta$), and high tunability of dielectric behaviors. The sintering temperature of BST prepared by conventional method is 1350–1400 °C [1], therefore, only platinum or refractory metals can be used as co-fired electrodes. These materials are usually expensive and their electrical performance is sometimes not satisfactory. So, reduction of the sintering temperature of BST is very necessary to enable BST to co-fire with cheaper and better electrical performance electrodes, such as Ag. Adding some glass component is sometimes useful in decreasing the ceramic sintering temperature [2]. In conventional method, glass was prepared in advance, then, mixed with the other starting materials [3,4]. In this paper, homogeneous gel-glasses of Ba–Sr–Ti–Pb–B–Si–O were prepared by sol–gel method without the glass preparation process beforehand. The effect of the composition and amount of glass addition on $Ba_xSr_{1-x}TiO_3$ was studied systematically.

The Curie temperature ($T_C$) of $BaTiO_3$ is 120 °C, while $SrTiO_3$ is paraelectric material without ferroelectric phase transition [5]. So, the Curie temperature of BST is adjustable. In the present study, the composition of $Ba_xSr_{1-x}TiO_3$ is fixed at $Ba_{0.7}Sr_{0.3}TiO_3$, that is, $x = 0.7$. Its Curie temperature is around room temperature.

## 2. Experimental procedure

The raw materials in this paper were: barium acetate ($Ba(AC)_2$), strontium acetate hemihydrate ($Sr(AC)_2\cdot(1/2)H_2O$), titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$), tributyl borate ($B(OCH_2CH_2CH_2CH_3)_3$), tetraethyl orthosilicate ($(C_2H_5O)_4Si$), acetic acid (HAC), and lead acetate trihydrate ($Pb(AC)_3\cdot3H_2O$). The sol–gel process used is described in Fig. 1.

The molar ratio of Ba:Sr:Ti adopted was 0.7:0.3:1. The barium acetate and strontium acetate were dissolved in acetic acid and stirred at 100 °C for half an hour. The described amount of titanium isopropoxide was added into the mixed solution of Ba–Sr when the solution cooled down to room temperature. On the other hand, the lead acetate was dissolved in acetic acid, then, tributyl borate and tetraethyl orthosilicate were mixed with lead acetate solution. These two kinds of solutions were mixed together

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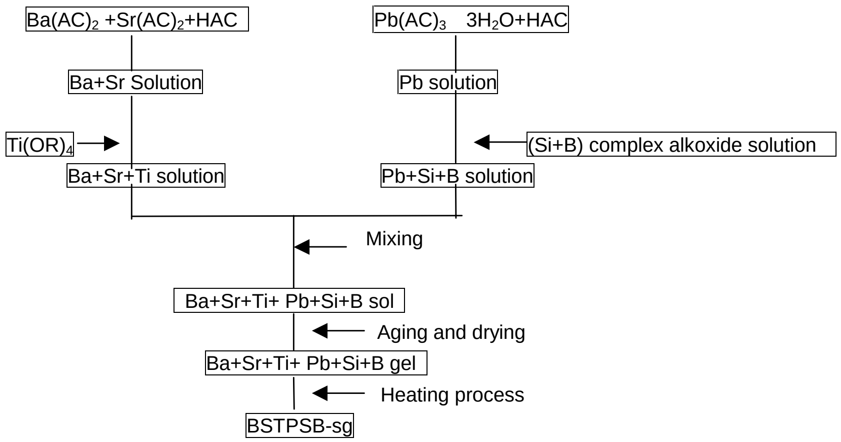

Fig. 1. Schematic illustration of the preparation procedures of the BSTPSB gel-glass.

Table 1
The doped compositions of BST samples

| Sequence number | Glass component | Composition (mol) |
|---|---|---|
| BST1-1 | $0.3PbO–0.23B_2O_3–0.47SiO_2$ (G1) | $0.88(Ba_{0.7}Sr_{0.3}TiO_3)\cdot 0.12$ (G1) |
| BST2-1 | $0.4PbO–0.05B_2O_3–0.55SiO_2$ (G2) | $0.88(Ba_{0.7}Sr_{0.3}TiO_3)\cdot 0.12$ (G2) |
| BST2-2 | | $0.75(Ba_{0.7}Sr_{0.3}TiO_3)\cdot 0.25$ (G2) |
| BST2-3 | | $0.6(Ba_{0.7}Sr_{0.3}TiO_3)\cdot 0.4$ (G2) |
| BST3-1 | $0.5PbO–0.04B_2O_3–0.46SiO_2$ (G3) | $0.88(Ba_{0.7}Sr_{0.3}TiO_3)\cdot 0.12$ (G3) |

and stirred for 60 min to form transparent and homogenous sol of Ba–Sr–Ti–Pb–B–Si–O. The sol transformed into gel by hydrolysis effect. The gel was dried at 200 °C and heat treated at 800 °C.

The compositions of different powders are given in Table 1.

The dry gel was analyzed by thermo-gravimetric analysis (TGA) and differential scanning calorimeter (DSC) (Thermal analyzer: NETZSCH STA449C, Germany). The crystal phase composition was studied by X-ray diffractometer (XRD) (D8 ADVANCE, Bruker, Germany). The microstructure was analyzed by scanning electron microscope (SEM) (Jeol JSM-5510, Japan) and dielectric property was measured by HP 4284A precision LCR meter.

## 3. Result and discussion

### 3.1. Sintering behaviors

XRD patterns of samples BST1-1, BST2-1, BST2-2, and BST3-1 treated at 800 °C and sample BST2-3 treated at 780 °C are shown in Fig. 2. The major crystal phase is perovskite BST. The diffraction peaks of major perovskite phase are strong and sharp. The small and weak peaks around 27.2° and 29.2° were proved to be the diffraction peaks of secondary phase ($BaTi_2Si_2O_8$) appearing in sample BST2-1 after annealed at 800 °C for 4 h. With increase of glass forming content, the other diffraction peaks of $BaTi_2Si_2O_8$ can be detected in BST2-2 and BST2-3, and the intensity of peaks become stronger which can be ascribed to the increasing of the secondary phase amount. As it can be found in this figure, the $BaTi_2Si_2O_8$ diffraction peaks almost cannot be detected in samples BST1-1 and BST3-1. The reason is perhaps that the content of Si was small in these two samples, which determined that the secondary phase content was too small to be detected. XRD pattern of BST2-2 sintered at 1025 °C shows that the diffraction peaks of secondary phase becomes stronger which indicates that the grains sizes of $BaTi_2Si_2O_8$ grew larger with increasing temperature.

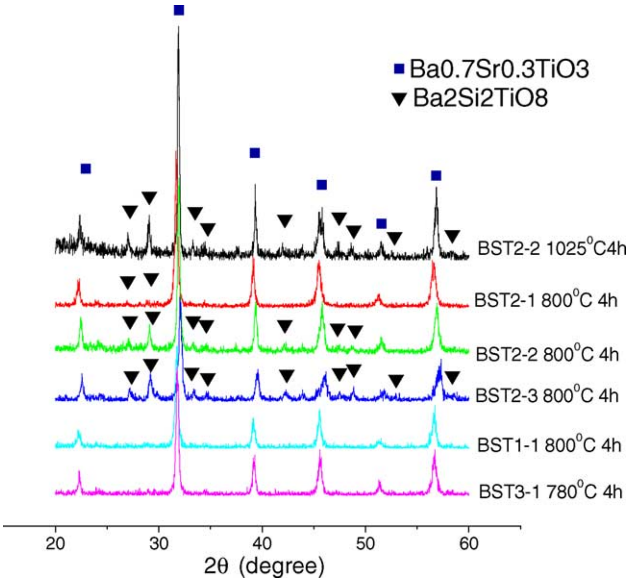

Fig. 2. XRD patterns of different compositions.

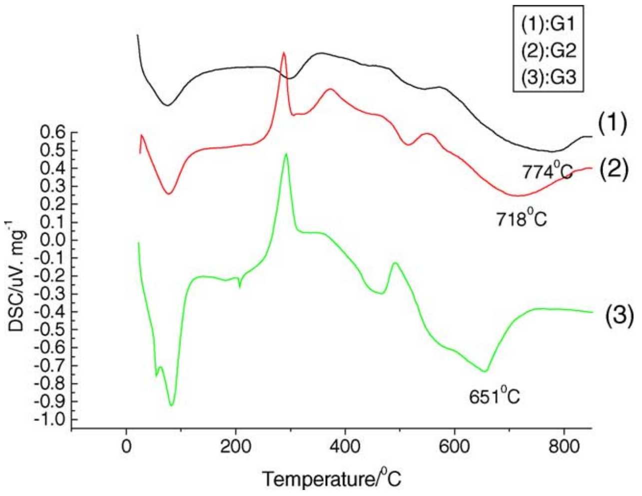

Fig. 3. DSC curves of G1, G2, G3.

The dry gels of G1, G2, and G3 prepared by sol–gel method were analyzed by DSC (Fig. 3). The melting points of G1, G2, and G3 decreased one by one (namely: G3 < G2 < G1).

Fig. 4a–e shows the scanning electron microstructure photographs of BST1-1, BST2-1, BST2-2, BST2-3, and BST3-1 which were sintered at 975 °C for 4 h. With the glass amount increasing, the densification of $Ba_{0.7}Sr_{0.3}TiO_3$ occurred at increasingly lower temperature. If the samples were sintered at same temperature, then the grain size would be larger (Fig. 4b–d). The grains of BST glass-ceramic grew larger with decreasing of glass melting temperatures, too (Fig. 4a, b and e). Fig. 4f shows, with sintering temperature increasing, needle-shape grains of secondary phase can be seen in BST2-2, and the result is the same as what is given in Fig. 2.

The relationships between bulk density, relative density, and sintering temperature are given in Fig. 5. Nearly full density (97.5%) was achieved in BST2-1 after being sintered at 1025 °C for 4 h. The relative densities of BST2-2 and BST2-3 were maximum when the sintering temperature were 1000 and 975 °C. So the sintering temperature of BST glass-ceramic was decreased with increasing of the glass forming content. The bulk density and relative density decreased with glass amount increasing (Fig. 5a). In addition, with the decreasing of glass melting point, the sintering temperature of BST glass-ceramic decreased which can be seen in Fig. 5b. The relationships between sintering temperatures and BST glass-ceramic compositions shown in Fig. 5 are the same as that shown in Fig. 4.

The results above demonstrated the sintering temperature of $Ba_{0.7}Sr_{0.3}TiO_3$ glass-ceramic prepared by sol–gel method can be decreased below 1000 °C through increasing the glass forming content and adopting correct BST glass-ceramic composition.

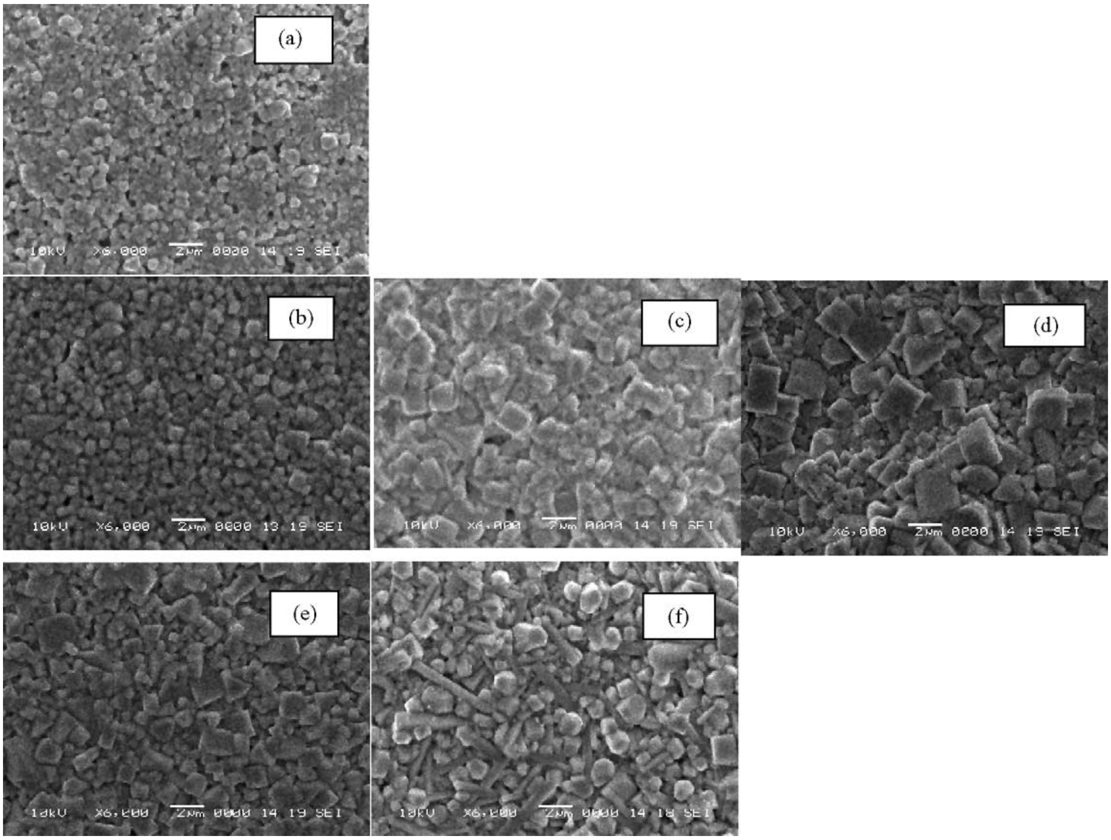

Fig. 4. SEM photographs of samples (a) BST1-1 975 °C 4 h, (b) BST2-1 975 °C 4 h, (c) BST2-2 975 °C 4 h, (d) BST2-3 975 °C 4 h, (e) BST3-1 975 °C 4 h, and (f) BST2-2 1025 °C 4 h.

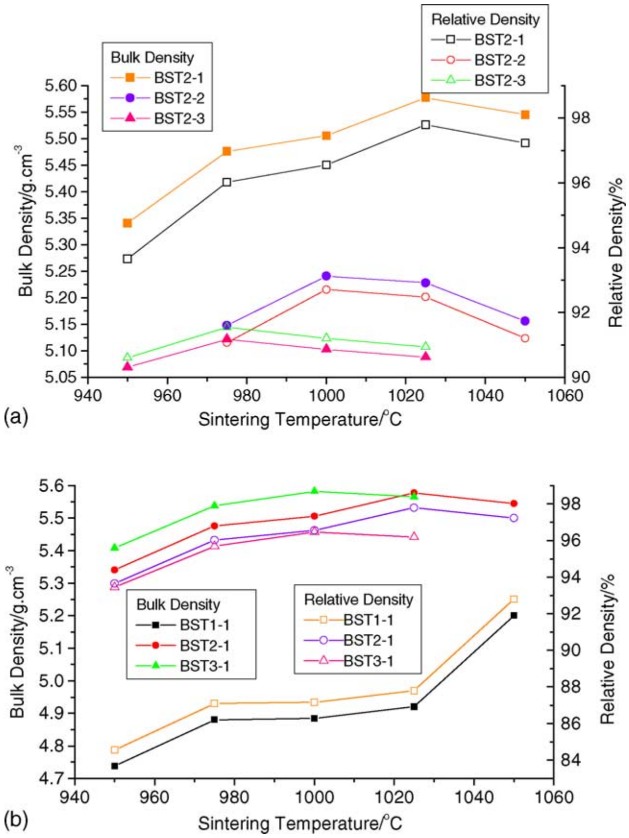

Fig. 5. Bulk density and relative density of samples.

### 3.2. Dielectric properties of BST glass-ceramic

The dielectric properties of BST glass-ceramics sintered at 1025 °C for 4 h were measured by HP4284A at 1 kHz (Fig. 6). The Curie temperature ($T_C$) of the pure $Ba_{0.7}Sr_{0.3}TiO_3$ ceramic is around room temperature. The Curie temperatures of BST glass-ceramics increased with increasing of $Pb^{2+}$ content, as it is shown in Fig. 6 ($T_C$: BST1-1 < BST2-1 < BST3-1 < BST2-2 < BST2-3). The reason is that $Pb^{2+}$ substituted $Ba^{2+}$ and $Sr^{2+}$ of the perovskite lattice forming $PbTiO_3$ and the Curie temperature of $PbTiO_3$ is about 490 °C. The amount of $PbTiO_3$ increased with $Pb^{2+}$ content increasing and the Curie temperatures of BST glass-ceramics increased with the amount of $PbTiO_3$ increasing. So, the more the $Pb^{2+}$ content, the higher the Curie temperature. The permittivity of glass is small, so the dielectric constant of $Ba_{0.7}Sr_{0.3}TiO_3$ glass-ceramic decreased with glass content increasing($\varepsilon$: BST2-1 > BST2-2 > BST2-3) (Fig. 6a). There were the same glass content in BST1-1, BST2-1, and BST3-1, but the permittivity of BST1-1 was less than that of BST2-1 and BST3-1, which can be ascribed to the lower relative density (Fig. 5) and the smaller average grain size (Fig. 4). Because the Curie temperatures shifted to higher temperatures, at room temperature the BST glass-ceramics was in ferroelectric state, then the dielectric loss at room temperature became larger (Fig. 6b).

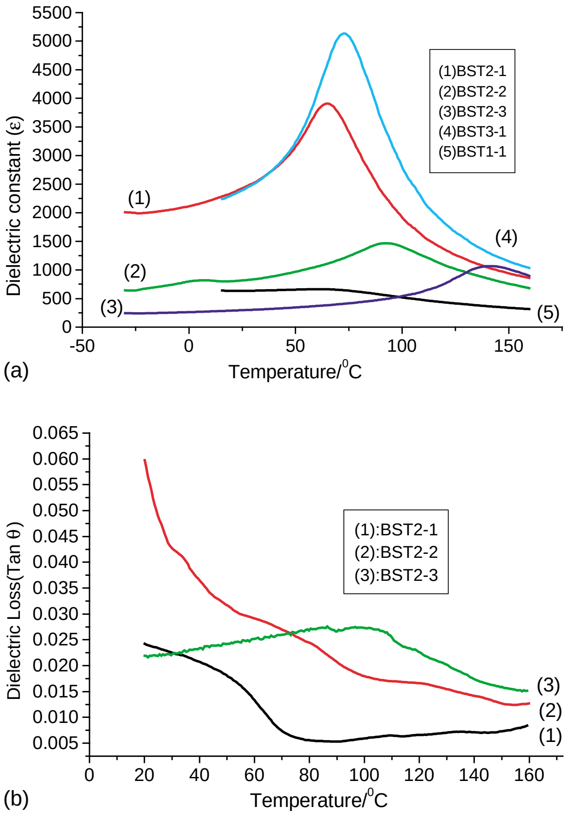

Fig. 6. The curves of $\varepsilon$–$T$ and $\tan\delta$–$T$.

## 4. Conclusions

In this paper, Ba–Sr–Ti–Pb–B–Si–O gel-glasses were prepared by sol–gel process. BST crystalline grains grew out from amorphous gel-glass matrix at proper heat treatment temperatures. The sintering temperatures of BST glass-ceramics decreased with the increase of glass content and the decreasing of glass melting temperature. Because $Pb^{2+}$ substituted $Ba^{2+}$ and $Sr^{2+}$ of the perovskite lattice forming $PbTiO_3$, the Curie temperature of BST glass-ceramic was higher than that of the pure $Ba_xSr_{1-x}TiO_3$. Because the Curie temperatures shifted to higher temperature, which decided that the BST glass-ceramics was in ferroelectric materials at room temperature, the dielectric loss at room temperature became larger. The permittivity of glass is small, so the dielectric constant of $Ba_{0.7}Sr_{0.3}TiO_3$ glass-ceramic decreased with increasing glass content.

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## References

[1] T. Hu, H. Jantunen, A. Uusimaki, S. Leppavuori, $Ba_{0.7}Sr_{0.3}TiO_3$ powders with $B_2O_3$ additive prepared by the sol–gel method for use as microwave material, Mater. Sci. Semicond. Process. 5 (2003) 215–221.

[2] N. Wang, M.-Y. Zhao, Z.-W. Yin, Low-temperature firing in microwave dielectric ceramic, J. Inorg. Mater. 17 (5) (2002) 915–924.

[3] D.-W. Kim, D.-G. Lee, K.S. Hong, Low-temperature firing and microwave dielectric properties of $BaTi_4O_9$ with Zn–B–O glass system, Mater. Res. Bull. 36 (2001) 585–595.

[4] H. Jantunex, R. Rautioaho, Compositions of $MgTiO_3$–$CaTiO_3$ ceramic with two borosilicate glasses for LTCC technology, J. Eur. Ceram. Soc. 20 (2000) 2331–2336.

[5] D. Bao, Z. Wang, W. Ren, Crystalline kinetics of $Ba_{0.8}Sr_{0.2}TiO_3$ sols and sol–gel synthesis of $Ba_{0.8}Sr_{0.2}TiO_3$ thin film, Ceram. Int. 25 (1999) 261–265.